ELECTROLESS PLATING METHOD USING FINE PARTICLES FIXED BY LIGHT AS CATALYST

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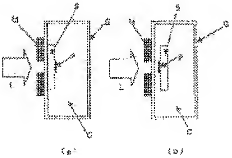
Abstract of **JP 2003013242** (A)
PROBLEM TO BE SOLVED: To provide a simple and efficient electroless plating technology which can form an electroconductive pattern on the surface of various kinds of substrate materials including a porous non-electroconductive material, and particularly can impart electroconductivity to the internal voids of the substrate materials.; SOLUTION: The electroless plating method comprises immersing the material to be electroless plated into a colloidel solution which has been prepared by means of dispersing the metal fine-perticles in a low polarity solvent, irradiating the meteriel with a laser light of an ultraviolet region to a near-infrared region to precipitete the metal fine-particles on the surface of the materiel to be electroless pleted end fixed them, end electroless plating the perts on which the metel fine-perticles are fixed by using the fixed metal fine-particle as a catalyst core. The non-electroconductive meterial having the formed electroconductive pettern cen be menufectured by meens of irradiating the non-electroconductive meterial to be electroless plated with the laser light eccording to a desired pettern.



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DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention]This invention belongs to the technical field of a surface treatment, and relates to the method of manufacturing the non-conducting material in which the specific conductive pattern useful as various kinds of high-performance material was formed, especially using a new electroless deposition method.
[0002]
[Description of the Prior Art]Electroless deposition is used as a method of metalizing the surface of insulating materials (non-conducting material), such as a plastic and glass, and giving conductivity. Typical electroless deposition is performed in the following procedures. (1) various kinds of etching methods -- the surface of plated material -- surface roughening -- and carry out hydrophilization (surface treatment). (2) Give the catalyst core of electroless deposition to plated material (core attachment processing), rank second to it, and activate the catalyst core (activation). (3) An electroless deposition coat is made to generate by being immersed in electroless plating liquid. Under the present circumstances, while a catalyst core acts as a catalyst for returning a metal ion and making it generate as a plated film, electroless deposition advances by having catalytic activity [the plated metal itself]. The catalyst core fixing method by making the surface treatment and the metallic colloid particles by vacuum ultraviolet light or radiation adsorb is also proposed.
[0003]When plating with the above techniques, plating usually advances on the whole surface of plated material. In order to patternize a field to be plated, before depositing metal on a catalyst pattern by electroless deposition, The paste which mixed to the photopolymer electroless deposition catalyst components, such as metal palladium which advances plating, is used, The method of forming the pattern of a catalyst bed by the photolithograph method, or fixing a catalyst core only to the exposed part by ultraviolet rays using a photosensitive palladium compound or photosensitive palladium polymer chelate is proposed. When a field to be plated was patternized to substrates, such as polyimide and glass, by these methods, there was much fixed down stream processing of a catalyst core, and there were problems, like a lot of waste liquid treatment, such as wash water, is required, and occurs.

[0004]For the purpose of, for example, obtaining a Teflon (registered trademark) porous electrode etc. As a method of forming a conductive pattern in the surface and the inside (surface of an inner hole) of a non-conductivity (non-conducting) porous material [chemical very inertness / polymers / fluorine system], When performing surface treatment / core attachment by :(1) solution which was insufficient in respect of the following as for the conventional technique, it is unable for a treatment area to attain to the whole porous material, and to form a conductive pattern only in a specific field inevitably. (2) the technique of fixing a catalyst core by the surface treatment and ultraviolet rays by vacuum ultraviolet light or radiation -- light and radiation -- the inside of a porous material -- and -- being hard -- since -- it is not suitable for the purpose of creating the conductive pattern which penetrates a thick porous material (about 1 mm or more). (3) the method of using a photosensitive material is difficult to remove [that the aperture of a porous material changes with the polymers which polymerized, or] an unreacted catalyst material thoroughly -- etc. -- there is a problem.

[0005]It is shown that heat is rapidly given with laser, some metaled vacuum evaporation films are wiped off as a formation method of a catalyst core required for electroless deposition, and it transfers on the charge of plating material these days (JP,2001-102724,A). however, this method is also inefficient in the point that it being unable to transfer inside the charge of plating material (surface of an inner hole) and a metal evaporated film are throwing away, only that part will be used as a catalyst core and the remainder will be discarded ---like -- it is -- carrying out -- noneconomic -- etc. -- there is a problem.

[0006]

[Problem(s) to be Solved by the Invention]The purpose of this invention can form a conductive pattern in the surface of various kinds of substrate materials containing a porous non-conducting material, and there is in providing the electroless deposition art new type [simple and efficient] which can also give conductivity especially to the hole of those insides.

[0007]

[Means for Solving the Problem]Previously, this invention persons thought out an optical fixing method of metal particles based on this phenomenon paying attention to metal particles depositing and adhering on the surface of a substrate, when a metallic colloidal solution was irradiated with a laser beam (Japanese Patent Application No. 11-342146; application for patent 2000-276369). By applying an optical fixing method of this metal particle to formation of a catalyst core in electroless deposition lately, this invention person established the electroless deposition method for the ability to attain the above-mentioned purpose, and drew this invention.

[0008]This invention immerses a charge of electroless deposition material in a colloidal solution which distributed and prepared metal particles to a low polar solvent as a basic invention in this way, By irradiating this with a laser beam of a near-infrared region from an ultraviolet area, deposit metal particles on the surface of said charge of electrolytic plating material, fix and by electroless deposition which uses fixed metal particles as a catalyst core. An electroless deposition method plating a portion to which metal particles

were fixed is provided.
[0009]This invention immerses non-conducting material in a colloidal solution which distributed and prepared metal particles to a low polar solvent as an invention using the above-mentioned electroless deposition method, By irradiating this with a laser beam of a near-infrared region from an ultraviolet area, according to a desired pattern, deposit metal particles on the surface of said non-conducting material, fix and by electroless deposition which uses fixed metal particles as a catalyst core. A manufacturing method of non-conducting material in which a conductive pattern was formed giving a method of giving conductivity only to a portion to which metal particles were fixed according to a desired pattern is provided. In one mode of a manufacturing method of non-conducting material in which a conductive pattern of this invention was formed, non-conducting material is a porous material and conductivity is also given to the surface of the inner hole.
[0010]
[Embodiment of the Invention]An embodiment of the invention is described in detail below in accordance with the component of this invention.
A. With the colloidal solution of the metal particles used by this invention, where the surface of a metal particle (5 nm - 50 nm) is preferably protected with a stabilizing agent which is preferably separated from the metal particle surface by laser beam exposure as for the particle diameter of 3 nm - 100 nm, distribute to a low polar solvent.
[0011]As metal which constitutes such a colloidal solution, the large metal of the plasmon absorption band in ultraviolet [, such as Ag, Au, Cu, Pd, and Pt,] - a near-infrared region can be mentioned as a desirable material. The particles of these metal absorb the energy of an ultraviolet - near-infrared laser beam, and deposit on the surface of a substrate (layer part). This invention is based on these metal with large plasmon absorption of ultraviolet - a near-infrared region having found out that it was metal which can have and carry out non-electrolytic deposition of the catalytic activity in electroless deposition, i.e., the catalytic activity over the oxidation of the reducing agent in electroless deposition, simultaneously.
[0012]As dispersion stabilizer which solubilizes metal particles, thiol compounds, such as dodecanethiol, can be mentioned to a low polar solvent. As a low polar solvent to distribute, hydrocarbon, such as aromatic series, such as alicyclic of aliphatic series, such as hexane, cyclohexane, etc., benzene, and toluene, is available. The viewpoint of avoiding degradation of the solvent by laser radiation to an alicyclic solvent is preferred.
[0013]B. Although the laser beam in particular used for fixing to a substrate face metal particles which were mentioned above is not limited and can use various kinds of laser beams of a near-infrared region from an ultraviolet area, especially use of a pulse laser beam is an efficient method. As a pulse laser beam, the thing of the fundamental wave (1064 nm) of Nd:YAG laser, a double wave (532 nm), three double waves (355 nm), 5 ns - 10 ns of pulse width and pulse energy 10mJ - 300mJ is useful, for example.
[0014]In optical immobilization of the metal particles by such laser beam exposure, generally, although the metal particles with large particle diameter have the high efficiency of optical immobilization, the dispersion stability in the inside of a low polar solvent worsens easily, particles condense, and it is easy to precipitate. That is, if the

metal particles of larger particle diameter are used, it is possible to fix particles with less irradiation energy. For example, if a particle with a mean particle diameter of 7.5 nm is used, although it is fixable with the irradiation energy more than about 18 $mJpulse(s)^{-1}cm^{-2}$ (532 nm, 10 ns), it receives, If a particle with a mean particle diameter of about 3 nm is used, unless it irradiates with the laser pulse more than $75mJpulse^{-1}cm^{-2}$ (532 nm) at least, immobilization of particles will not take place. On the other hand, the metal particles with large particle diameter have the bad dispersion stability in the inside of a low polar solvent, and since particles condense and it is easy to precipitate, to the mothball (about one month or more) of a solution, it is unsuitable. It is preferred that metal particles generally set to 100 nm or less as mean particle diameter in consideration of these points. Although the minimum of the particle diameter of metal particles does not consist especially theoretically, considering the facilities on use of laser which was mentioned above, it is preferred to be referred to as not less than 5 nm as mean particle diameter generally. The metal particles to which it stuck weakly physically except the laser radiation part can be removed nearly thoroughly by being immersed in solvents, such as cyclohexane used for distribution of metal particles which were mentioned already.

[0015]C. Drawing 1 explains to the surface of a substrate theoretically a deposit and the process to fix of metal particles from the colloidal solution of metal particles according to this invention. A pulse laser beam (L) is irradiated via a mask (M) by the metallic colloidal solution (C) by which the substrate (S) is immersed in the cell (G). Metal particles (P) are fixed to the surface of the irradiated substrate (S). The process of immobilization of metal particles can be carried out also by operating a laser beam according to a desired drawing figure (pattern) via a mask. When a substrate is transparent, the method (b) which the method (a) of sticking a substrate in a glassware wall and irradiating with it separates from a container wall about 1-3 mm and with which it irradiates in being opaque is effective.

[0016]D. In this invention, when the metal particles which serve as a catalyst core as mentioned above immerse the substrate by which optical immobilization was carried out in chemical-plating liquid, carry out electroless deposition. Chemical-plating liquid in particular is not limited and various kinds of chemical-plating liquid containing metal salt and a reducing agent for electroless deposition can be used for it.

[0017]As metal (plated metal) contained in chemical-plating liquid, it is usable in all of the metal known as metal of non-electrolytic deposition nature from the former, such as Au, Ag, Cu, Pd, Pt, nickel, and Co. Any of the metal of metal, congener, or another ** which were beforehand fixed on the substrate as a catalyst core as mentioned above may be sufficient as the metal contained in chemical-plating liquid. As a reducing agent contained in the chemical-plating liquid for electroless deposition, although formaldehyde (formalin), hypophosphite, etc. are mentioned, it is not limited to these, for example.

[0018]If this invention is followed as mentioned above, metal particles are fixed on the surface of the substrate (non-conducting material for plating) by laser beam exposure

from the colloidal solution, By performing electroless deposition by using this metal particle as a catalyst core, predetermined metal can be plated and the non-conducting material in which the conductive pattern was formed can be manufactured by irradiating with a laser beam according to a desired pattern in this case.

[0019]Since it will irradiate with a laser beam where the non-conducting material for plating (substrate) is immersed into the colloidal solution of metal particles if this invention is followed, the metal particles used as a catalyst core are uniformly fixed to a substrate according to a desired pattern, and, as a result, uniform plating is attained by the next electroless deposition process. A conductive pattern which penetrates a thick porous material can also be given without fixing the metal particles used as a catalyst core even to the surface of the inner hole, therefore plating advancing certainly even to an inner hole, and spoiling the porosity, especially when non-conducting material is a porous material.

[0020]If this invention is followed, the metal particles in a colloidal solution will hardly change except a laser radiation portion, but if a constant rate of solutions are put in the irradiation cell, it is usable to immobilization of a repetition catalyst core, and they can be plated very efficiently (economical). In the electroless deposition according to this invention, a catalyst core can be formed in a colloidal solution which was mentioned above by easy operation of irradiating with a short-time (for example, 60 or less seconds) laser beam, and complicated pretreatment or waste liquid treatment are not needed for it.

[0021]As a non-conducting material which can fix the metal particles used as a catalyst core according to this invention, can plate the metal of non-electrolytic deposition nature, and can form a required conductive pattern, In addition to inorganic materials, such as glass, calcium fluoride, and single crystal silicon, various kinds of polymer, such as polymethylmethacrylate, polyvinyl chloride, and fluorine system polymers (Teflon), is mentioned.

[0022]The electroless deposition method for following this invention is useful also although the surface (the surface of an inner hole is included) of a porous material is plated. Conductivity can be given without spoiling most porosity, even if the membrane filter of fluorine system polymers is available as an example of a porous material and it is a substrate of 100 nm or less of average pore sizes. Hereafter, in order to show the feature of this invention still more concretely, an example is described, but this invention is not restricted by these examples.

[0023]

[Example](1) The gold colloid solution was obtained by the method (J. Phys. Chem., 99, and 7036 (1995)) of reflex (Leff) and others of returning the preparation chloroauric acid of the plating A. gold colloid solution to a membrane filter with sodium borohydride. As a result of measuring with a transmission electron microscope (TEM), the mean particle diameter of golden particles was 7-8 nm.

[0024]B. the optical fixing method of the golden particles to a membrane filter -- the gold colloid produced as mentioned above was dissolved in cyclohexane, and it was considered as the colloidal solution. This solution abbreviation 3mL is put into the quartz cell (4x1x4 cm) for fluorometry, The membrane filter made from Teflon (Millipore Corp.

DEYURAPOA VVLP, 0.1 micrometer in aperture) was dipped, and it irradiated with the pulse laser beam (Nd: an YAG laser, the wavelength of 532 nm, the pulse width of 5-7 nm, the about 33 pulse energy mJ(s), repetition number of 10 Hz) for about 30 seconds. The mask was placed all over the cell, and a laser beam passes this mask and was made to carry out the pattern exposure of the membrane filter (drawing 1). When the membrane filter was taken out and cyclohexane washed, adhesion of golden particles was checked by only the laser beam irradiation part. The membrane filter was immersed into toluene and desorption was not clearly accepted by ultrasonic irradiation. That is, it was checked that golden particles are incorporated into the inner hole of a membrane filter. Drawing 2 is a scanning electron micrograph (SEM image) of the golden particles fixed corresponding to the mask. The round white thing was the gold colloid deposited and fixed, and particle diameter was about 10 nm to about 60 nm. It is guessed that the difference in particle diameter is a thing also depending on the particle size distribution of the golden particles before a laser beam exposure.

[0025]C. The membrane filter (pore size, 100 nm) in which the electroless deposition gold nano particle was fixed was dipped in the plating solution for 40 minutes. A plating solution mixes the solution which diluted formalin 2mL in the solution which melted a potassium sodium tartrate (0.7g) and copper sulfate (2.0g) in water (40mL) with water, and was used as it at 10mL just before use. It is usable also in a commercial plating solution. The membrane filter was taken out and it was air-dry after rinsing. It checked with the tester that the plated portion (portion of the heart shape of drawing 3) was conductivity. The scanning electron microscope photograph of the plating portion of a membrane filter is shown in drawing 4. The porous structure to which the fiber lapped with mesh shape is a structure peculiar to a membrane filter, and it turned out that it is going on inside a filter surface and porous structure (surface of an inner hole) so that a metal skin may cover a fiber. It turned out that the porosity of a membrane filter is considerably maintained after plating treatment in this case.

[0026](2) In the same way as the plating membrane filter to a glass substrate, electroless deposition was performed about what fixed golden particles for the cover glass (0.1 mm in thickness) on the surface. Conductivity was checked about the portion of the heart shape of drawing 5. From the plated scanning electron microscope photograph (drawing 6) of the portion, it became clear that copper of thickness with a mean number of 10 micrometers - hundreds of micrometers is plated.

[0027]

[Effect of the Invention]As stated above, it is not limited to a substrate material by short-time laser radiation, but fixes to various kinds of non-conducting materials by it according to the pattern of a request of the metal particles used as the catalyst core of electroless deposition, and this invention makes it possible further to create the electric conduction part by electroless deposition simple. This invention serves as a means excellent in the pattern formation of the functional porous electrode used for creation, electrochemical sensors, and the cell of the metal detailed line pattern used for a semiconductor device, a semiconductor device mounting component, various flat panel display devices, optical devices, etc.

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CLAIMS

[Claim(s)]
[Claim 1]A charge of electroless deposition material is immersed in a colloidal solution which distributed and prepared metal particles to a low polar solvent, An electroless deposition method which deposits metal particles on the surface of said charge of electrolytic plating material, is fixed and is characterized by plating a portion to which metal particles were fixed by electroless deposition which uses fixed metal particles as a catalyst core by irradiating this with a laser beam of a near-infrared region from an ultraviolet area.
[Claim 2]Non-conducting material is immersed in a colloidal solution which distributed and prepared metal particles to a low polar solvent, By irradiating this with a laser beam of a near-infrared region from an ultraviolet area, according to a desired pattern, deposit metal particles on the surface of said non-conducting material, fix and by electroless deposition which uses fixed metal particles as a catalyst core. A manufacturing method of non-conducting material in which a conductive pattern was formed carrying out addition of conductivity only to a portion to which metal particles were fixed according to a desired pattern.
[Claim 3]A manufacturing method of non-conducting material in which non-conducting material is a porous material, and a conductive pattern was formed in claim 2 also giving conductivity to the surface of the inner hole.

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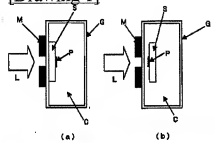
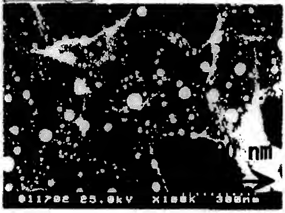
DRAWINGS

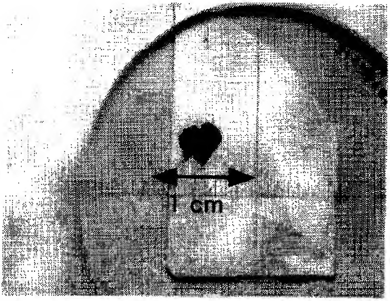
[Drawing 1]



[Drawing 2]



[Drawing 3]



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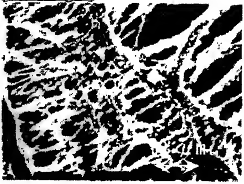
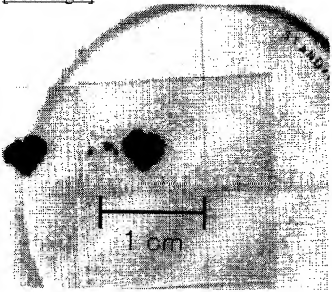


[Drawing 5]



[Drawing 6]

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